

DERWENT-ACC-NO: 1983-801692

DERWENT-WEEK: 198344

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TITLE:

Coloured decorative patterns applied to glass or ceramic prods. - esp. where pigment suspension applied to prod. is exposed to laser beam to obtain inexpensive filigree pattern

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PRIORITY-DATA: 1981DD-0233153 (September 9, 1981)

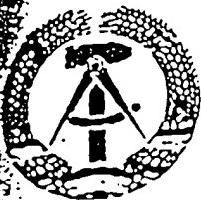
PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
DD 201136 A	July 6, 1983	N/A	005	N/A

IPC: C03C017/00

ABSTRACTED-PUB-NO:DD 201136A

BASIC-ABSTRACT: An object made of glass or ceramic is coated with a pigment. The coating is then exposed to a finely-focussed laser beam with an output of 20-200 watts, so a coloured pattern can be fixed on the object without removing any material from the glass or ceramic. The laser lens is pref. moved along a desired path or through a template to form the desired decorative pattern. The coloured pigments are pref. metal -salts, -oxides, or -nitrides; or coloured frits. The pigments are pref. applied as a suspension by painting; by spraying solns.; by spraying powder onto an object coated with binder; or by electrostatic spraying after coating the object with a conducting layer.



PATENTSCHRIFT

201 136

ISSN 0433-8461

(11)

Int.Cl.³

3(51) C 03 C 17/00

AMT FUER ERFINDUNGS- UND PATENTWESEN

In der vom Anmelder eingerichteten Fassung veröffentlicht

(21) WP C 03 C / 2331 534

(22) 09.09.81

(44) 06.07.83

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(73) siehe (72)
(74) ADW DER DDR ZI F. KERNFORSCHUNG PATENTBUERO 8051 DRESDEN PSF 19

(54) VERFAHREN ZUR HERSTELLUNG FARBIGER DEKORE AUF GLAS- ODER KERAMIKARTIKELN

(57) Die Erfindung betrifft ein Verfahren zum Aufbringen von farbigen filigranen Dekoren zur Veredlung von Glas- und Keramikartikeln. Mit der Erfindung soll eine Veredlung von Glas- und Keramikartikeln durch Aufbringen abriebfester filigraner farbiger Dekore auf möglichst wirtschaftliche Weise unter Verwendung der Lasertechnik geschaffen werden. Ernungsgemäß wird dazu der Glas- oder Keramikartikel mit färbenden beziehungsweise gefärbten Stoffen, wie Metallocide, Metallnitride, Farbfritten, Metallsalze, beschichtet und durch Einwirkung eines dem auszubildenden Dekor entsprechend geführten fein-fokussierten Laserstrahls einer Outputleistung von 20–200 Watt fixiert, ohne daß dabei ein Materialabtrag auf dem zu dekorierenden Gegenstand erfolgt.

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Anwendungsgebiet der Erfindung

Die Erfindung betrifft ein Verfahren zum Aufbringen von farbigen filigranen Dekoren zur Veredlung von Glas- und Keramikartikeln.

Charakteristik der bekannten technischen Lösungen

Zur Herstellung von farbigen Dekoren auf Gläsern und Keramikartikeln verwendet man größtenteils die Siebdrucktechnik. Siebdruckdekore haben den Nachteil, daß sie nur eine geringe Resistenz gegen mechanische und mechanisch-chemische Beanspruchung speziell beim Reinigen der dekorierten Artikel nach Gebrauch aufweisen. Außerdem ist die Siebdrucktechnik meist auf ebene Flächen begrenzt.

Durch Schleifen, Schneiden oder Ätzen farbig überfangener Gläser lassen sich farbige Negativdekore herstellen. Filigrane Schmuckdekore auf Glas- oder Keramikartikeln fertigt man vorteilhaft durch Gravur mittels Laserstrahlen (z.B. DD-PS 118251). Zur Herstellung farbiger filigraner Positivdekore ist diese Lasertechnik nicht anwendbar.

In der japanischen Patentschrift IA 49-4352 wird ein Laser-dekorationsverfahren zur Herstellung farbiger Bilder auf Glas- oder Keramikartikeln vorgeschlagen, bei dem das vorgesehene farbige Bild insgesamt auf den zu dekorierten Artikel aufgebracht und anschließend mittels eines Laserstrahls fixiert wird, der die gesamte Bildfläche unmittelbar ausleuchtet. Der Nachteil dieses Verfahrens besteht darin, daß einmal das gewünschte Bild nur auf ebenen Flächen mittels Siebdruck aufgebracht werden kann, ansonsten von

Hand aufgemalt werden muß und zum anderen zur anschließenden Fixierung ein energieintensiver Laser extrem hoher Leistung mit einem der Bildfläche entsprechenden Strahlungsdurchmesser erforderlich ist, der beim heutigen Stand der Lasertechnik einen hohen finanziellen Aufwand erfordert, so daß eine wirtschaftliche Prozeßführung auf diese Weise nicht möglich ist.

Ziel der Erfindung

Ziel der Erfindung ist eine Veredlung von Glas- und Keramikartikeln durch Aufbringen abriebfester filigraner farbiger Dekore auf möglichst wirtschaftliche Weise.

Darlegung des Wesens der Erfindung

Der Erfindung liegt die Aufgabe zugrunde, ein Verfahren zur Herstellung filigraner gravurähnlicher farbiger Positivdeko re unter Verwendung der Lasertechnik zu schaffen.

Erfundungsgemäß wird dazu der Glas- oder Keramikartikel mit färbenden beziehungsweise gefärbten Stoffen, wie Metalloxide, Metalluitride, Farbfritten, Metallsalze, beschichtet und durch Einwirkung eines dem auszubildenden Dekor entsprechend geführten fein-fokussierten Laserstrahls einer Outputleistung von 20-200 Watt fixiert, ohne daß dabei ein Materialabtrag auf dem zu dekorierenden Gegenstand erfolgt. Das fargebende Pigment kann außer in Form einer Suspension auch durch Aufstäuben auf den mit einer Bindemittelschicht überzogenen Artikel aus Glas oder Keramik oder durch elektrostatischen Auftrag auf den mit einem leitfähigen Überzug versehenen Artikel aufgebracht werden.

Ausführungsbeispiele

Die Erfindung wird durch folgende Ausführungsbeispiele noch näher erläutert, wobei die Erfindung nicht auf diese Bei-

spiele beschränkt ist.."

Beispiel 1

Ein farbloses Stielglas wurde auf einem Drehteller langsam um seine Längsachse gedreht. Mittels einer entsprechenden Düse wurde ein 20mm breiter Streifen des Kelches mit einer CoO-haltigen Suspension beschichtet. Nach der Beschichtung wurde der auf einen Brennfleck von $0,25\text{mm}^2$ fein-fokussierte Strahl eines 200 Watt-CO₂-Lasers mit Hilfe eines Sägezahnimpulsgebers über die 20mm breite Fläche gewobbelt, so daß ein filigranes mäanderartiges dunkelblaues Dekor auf dem Glas entstand. Die restliche Suspension wurde abgewaschen und der Wiederaufarbeitung zugeführt.

Beispiel 2

Ein Stangenglas wurde 20mm unterhalb des Lippenrandes mit einer ca. 40mm breiten Bindemittelschicht beschichtet. Anschließend wurde eine dunkelgrüne Farbglasfritte aufgestäubt. Über das Glas wurde eine Metallmaske mit einem Weinlaubmuster geschoben. Anschließend wurde die Metallmaske auf einem Drehteller durch langsames Anheben mittels des unter Beispiel 1 beschriebenen Lasers abgerastert. Nach dem Abnehmen der Maske und dem Entfernen der überschüssigen Farbfritte inclusive Bindemittel zeigte das Glas ein scharf gezeichnetes dunkelgrünes Weinlaubdekor, wie es durch die Metallschablone vorgegeben wurde.

Beispiel 3

Eine flache Keramikschale wurde mit einer braunen Schmelzfarbensuspension beschichtet und anschließend auf einem Drehteller langsam gedreht. Der Strahl des unter Beispiel 1 beschriebenen Lasers wurde mechanisch gewobbelt und erzeugte auf der Wandfläche der Keramikschale ein sinuswellenförmiges dunkelbraunes filigranes Muster. Die unverbrauchte Schmelzfarbe wurde wieder entfernt.

Die nach der Erfindung hergestellten Dekore zeigten eine gegenüber dem Siebdruck wesentlich höhere Abriebfertigkeit, so daß selbst nach mehrfachen maschinellen Reinigen der Glas- bzw. Keramikartikel keinerlei Fehlstellen im Dekor vorhanden waren.

Erfindungsanspruch

1. Verfahren zum Aufbringen farbiger Dekore auf Glas- oder Keramikartikeln dadurch gekennzeichnet, daß farbgebende Pigmente auf den zu dekorierenden Artikel aufgebracht und anschließend unter Verwendung eines feinfokussierten Laserstrahls einer Outputleistung von 20-200 Watt, der in dem auszubildenden Dekor entsprechender Weise geführt wird, in den Glas- oder Keramikartikel fixiert wird, ohne daß ein Materialabtrag auf dem zu dekorierenden Gegenstand erfolgt.
2. Verfahren nach Punkt 1, dadurch gekennzeichnet, daß die Führung des Laserstrahles durch eine zwischen die Laserquelle und den zu dekorierenden Artikel eingebrachte Schablone oder eine steuerbare Linse erfolgt.
3. Verfahren nach Punkt 1, dadurch gekennzeichnet, daß als farbgebende Pigmente Metallsalze, -oxide, -nitride oder Farbfritten verwendet werden.
4. Verfahren nach Punkt 1, dadurch gekennzeichnet, daß das Aufbringen der farbgebenden Pigmente durch Beschichten mit einer Suspension, durch Aufsprühen entsprechender Lösungen, durch Aufstäuben von Pulvern geeigneter Körnung auf vorher mit Bindemittel beschichteten Artikeln oder durch elektrostatischen Auftrag auf den mit einem leitfähigen Überzug versehenen Artikel erfolgt.

German Democratic Republic

PATENT

Economic Patent

ISSN 0433-6461 (11) 201 136

Granted as per § 6, Section 1 of Amending Law
to the Law on Patents Int. Cl.³ 3(51) C 03 C 17/00

Office for Inventions and Patents Published in the version submitted by the applicant

(21) WP C 03 C / 2331 534 (22) 09/09/81 (44) 07/06/83

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(64) PROCESS FOR PRODUCING COLOR DECORATIONS ON GLASS OR
CERAMIC ARTICLES

(57) The invention relates to a process for applying filigree color decorations for refining glass and ceramic articles. The invention provides a refinement process for glass and ceramic articles by applying abrasion-resistant filigree color decorations by the most economical method possible using laser technology. In accordance with the invention, the glass or ceramic article is coated with chromophore or stained substances, such as metal oxides, metal nitrides, color frits, or metallic salts, which are fixated by the effect of a fine-focused laser beam having an output of 20 - 200 Watts and guided so as to correspond to the decoration to be applied without removing any material from the decorated object.

Field of Application for the Invention

The invention relates to a process for applying filigree color decorations for refining glass and ceramic articles.

Characteristics of the Previously Known Technical Solutions.

The primary technology used for producing color decorations on glass or ceramic articles is the screen printing process. Screen printed decorations have the disadvantage of exhibiting low resistance to mechanical and mechanical-chemical strains, particularly when the decorated articles are cleaned after use. Moreover, the screen print technology is usually limited to flat surfaces. Negative color decorations are produced by grinding, cutting or etching color plated glass. Filigree decorations on glass or ceramic articles are advantageously produced by means of an engraving process with the use of a laser beam (for example DD-PS 118251). This laser technology is not suitable for producing filigree color positive decorations.

The Japanese patent IA 49-4352 proposes a laser decoration process for producing colored pictures on glass or ceramic articles, whereby the intended color picture is applied completely to the article to be decorated and subsequently fixated by means of a laser beam, which directly illuminates the complete picture area. One of the disadvantages of this process is that the desired picture is applicable only to flat surfaces by means of the screen printing process, or else it must be hand-painted. The other is that, in order to subsequently fixate the picture, an energy-intensive extremely high capacity laser is required, having a radiation diameter that corresponds to the picture area.

Based on the current state of laser technology this results in high financial expenditures thereby making an economical process impossible with the use of this method.

Object of the Invention

The object of the invention is to refine glass and ceramic articles by applying abrasion-resistant filigree color decorations by the most economical method possible.

Description of the Nature of the Invention

The invention is based on the object to provide a process for producing filigree engraving-like positive color decorations with the use of laser technology.

In accordance with the invention, the glass or ceramic article is coated with chromophore or stained substances, such as metal oxides, metal nitrides, color frits, metallic salt, which are fixated by the effect of a fine-focused laser beam having an output of 20 - 200 Watts and guided so as to correspond to the decoration to be applied without removing any material from the decorated object. The chromophore pigment is applied either in the form of a suspension, by dusting it onto the glass or ceramic article which is coated with a bonding agent, or by electro-static application to the article which is provided with a conductive coat.

Exemplary Embodiments

The invention is described in more detail by means of the following exemplary embodiments. The invention is not limited to these examples, however.

Example 1

A colorless stemmed glass was slowly rotated about its longitudinal axis on a rotary table. Using an appropriate nozzle, a 20 mm wide strip on the cup was coated with a CoO-containing suspension. Following the coating process the beam of a 200 Watt CO₂ laser, which was fine-focused to a linear focus of 0.25 mm², was wobbled over the 20 mm wide surface by means of a saw tooth pulse generator, thereby producing a filigree meandering dark blue decoration on the glass. The remaining suspension was washed off and reconditioned.

Example 2

20 mm below its lip, a tall glass was coated with a bonding agent layer having a width of approx. 40 mm. Subsequently a dark green stained-glass frit was dusted on. A vine-patterned metal mask was slid over the glass, and the metal mask was subsequently slowly lifted on a rotary table while being scanned by the laser described in Example 1. When the mask and the excess color frit including the bonding agent were removed, the glass was found to have a sharply defined dark green vine pattern decoration as per the metal template.

Example 3

A flat ceramic bowl was coated with a brown enamel color suspension and subsequently slowly rotated on a rotary table. The beam of the laser described in Example 1 was mechanically wobbled and produced a sine wave-like dark brown filigree pattern on the wall surface of the ceramic bowl. The unused enamel was removed.

Compared with the screen printing process, the decorations produced in accordance with the invention exhibited a significantly higher abrasion resistance. Even after being cleaned multiple times, the decoration on the glass and ceramic articles showed no defects.

Patent Claims

1. Process for applying color decorations to glass or ceramic articles, characterized in that chromophore pigments are applied to the article to be decorated and subsequently fixated on the glass or ceramic article with the use of a fine-focused laser beam having an output capacity of 20 - 200 Watts and guided so as to correspond to the decoration to be applied without removing any material from the object to be decorated.
2. Process pursuant to 1 above, characterized in that the laser beam is guided by a template placed between the laser source and the article to be decorated or by a controllable lens.
3. Process pursuant to 1 above, characterized in that the chromophore pigments are metal salts, metal oxides, metal nitrides or color frits.
4. Process pursuant to 1 above, characterized in that the chromophore pigments are applied in the form of suspension coating, by spraying on respective solutions, by dusting powders of suitable graining onto articles that were previously coated with a bonding agent, or by electro-static application to the article that was previously provided with a conductive coat.

Translation patent Nr. 201 136

The invention concerns on a process for adding a coloured, filigran decoration on glass and or ceramic to ennoble the surface of these materials. The intention of the invention is to ennoble glass and or ceramic surfaces by adding a rub resistant, filigran and coloured decoration with the help of laser energy to get a more economically process. Therefore the glass and or ceramic material is coated with stained or rather coloured material, like metal oxides, metal nitrates, coloured fritts or metal salts. By the influence of a fine-focused, to the decoration corresponding steered laser beam, with an output power between 20 and 200 watts, the material will be fixed without damaging the surface of the decorating part.

application areas of the invention

The invention refers to a process for adding coloured, filigran decorations on glass and or ceramic to ennoble the surface of these materials

characteristic of well-known technical solutions

for the production of coloured decorations on glass and or ceramics you normally use the silk screen printing technology. The disadvantage of the printing technology is that you only have little resistance to mechanical and mechanical-chemical stress, especially during the cleaning of the materials after their usage. Moreover the silk screen technology is limitated to plan surfaces.

Using grinding, cutting or etching technologies you are able to produce negative decorations on colour-coated glasses. For the production of filigran decorations on glass and or ceramic surfaces you normally engrave the material with a laser beam (for example patent DD-PS 118 251). It is not possible to use the laser technology for the production of coloured, filigran positive decorations.

A japanes patent (JA 49-4352) describes a process for a laser decoration of glass and or ceramic surfaces, printing the whole coloured picture on the surface of the material which should be decorated. Afterwards the whole picture is illuminated with a laser beam and so fixed to the glass and or ceramic surface.

The first disadvantage of this process is that you only can print (silk screen) the picture on plan surfaces. A decoration of uneven surfaces is only possible by hand painting.

The second disadvantage is that you have to use an extremely high powered laser beam which must have the size of the whole picture. At the moment these lasers are very expensive and therefore an economically process control is not possible.

intention of the invention

The intention of the invention is to ennoble glass and or ceramic surfaces by adding a rub resistant, filigran and coloured decoration in a most economically way.

Idea of the invention

The task of the invention is to create a process for the decoration of filigran, most similar to an engraving, coloured decoration of glass and or ceramic surfaces in a most economically way.

In refer to the invention, the glass and or the ceramic material therefore is coated with stained or rather coloured material, like metal oxides, metal nitrates, coloured frits or metal salts. By the influence of a fine-focused, to the decoration corresponding steered laser beam, with an output power between 20 and 200 watts, the material will be fixed without damaging the surface of the decorating part. The colouring pigment can be added to the surface in the form of a emulsion or by spraying the pigment on the material, which first has to be coated with a solvent, or by a electrostatic process, for which the material first has to be coated with a conducting carrier.

application examples

The invention will be explained with the following examples, but is not only limitated on these examples.

example 1

A colourless drinking glass with a handle was slowly spined around ist longitudinal axis with the help of a rotating table unit. With a corresponding nozzle a 20mm wide belt of CoO emulsion was coated on the surface of the glass. After the coating a 200watt CO₂-laser was focused (spot size 0,25 mm²) onto the surface of the glass. The laser beam (sägezahnimpuls= impulse for one of the mirrors) was wobbled over the 20mm wide area. As result you obtained a filigran dark blue decoration like a mäander on the surface of the glass. The rest of the emulsion was wiped off and recycled.

example 2

A glass tube was coated with a 40mm wide belt of solvent, 20mm underneath the edge. Afterwards a dark green coloured glas frit was sprayed onto the solvent. Then a metal mask with a pattern was put over the solvent belt. In the next step the metal mask was scaned with the laser described in the paragraph above, while spining the glass with the rotating table unit and moving the laser unit in the longitudinal axis up and down. After removing the metal mask and wiping of the rest of the colour frit including the solvent, the glass showed the sharp dark green picture of the pattern set by the metal mask.

example 3

A flat ceramic bowl was coated with a brown melting colour emulsion and slowly spined with the rotating table unit. The beam of the laser, as discribed in the first paragraph, was mechanically wobbled over the surface of the bowl and produced a filigran dark brown pattern like a sinus wave on the surface of the bowl. The rest of the melting colour was wiped off once again.

In comparison with the silk screen printing technology, the decorations made with the described invention were much more rub resistant. There were no damages in the decorations, even after several mechanical cleaning cycles.

claims of the invention

1. process for coloured decoration of glass and or ceramic surfaces with the characteristic that the pigments which causes the decoration colour were added to these surfaces and afterwards fixed by a fine-focused laser beam with an output power between 20 and 200 watts. The laser beam is steered corresponding to the nature of the decoration. The decoration material (pigments) will be fixed without damaging the surface of the part, which should be decorate.
2. process described as in paragraph 1. with the characteristic that the beam steering between laser source and the part which should be decorate can be made with a mask or a controlled reflection lens.
3. process described as in paragraph 1. with the characteristic that the pigments which causes the decoration colour can be made of metal salts, metal oxides, metal nitrides or coloured frits
4. process described as in paragraph 1. with the characteristic that the addition of pigments which causes the decoration colour can be made by coating or spraying on an emulsion, spraying on powders with the right granulation, after the parts were coated with a solvent or by an electrostatic process after the parts were coated with a conductive layer.

German Democratic Republic Patent 201 136 (2331534)

Akademie der Wissenschaften der DDR. [Academy of Science of East Germany]

Inventors: Boden, Gotfried; Koutsch, Andreas; Richter, Edgar; Staedtler, Ludwig; Poitz, Tilo;
Schulz, Hans-Jurgen; Uhlmann, Alfred.

Title: **Process for the Manufacture of Colored Decorations on Glass and Ceramic Articles.**

Summary

- (7) This invention involves a process for creating colored filigree decorations for the enhancement of glass and ceramic articles. With the invention, the enhancement of glass and ceramic articles should be by application of an abrasion-resistant filigree of colored decoration in a way as is as economical as possible by the use of laser-technology. In accordance with this invention, glass or ceramic articles are coated with coloring, as well as colored, materials such as metal oxides, metal nitrides, color frits, metal salts, and leading to the decoration to be formed, are fixed by the effect of a fine-focused laser beam with an output power of 20-200 watts, without which a material damage takes place on the object to be decorated.

Application area this invention.

This invention involves a process for the application of decorations of colored filigrees for the enhancement of glass and ceramic articles.

Description of the known technical solutions.

For the manufacture of colored decorations on glass and ceramic articles, one uses mainly screen printing technology. Screen printing decoration has the disadvantage that they have only a low resistance against mechanical and mechanical-chemical requirements which appear specifically with the cleaning of the decorated articles after use. Furthermore, the screen printing technology is usually restricted to flat surfaces.

By grinding, cutting or etching of colored thin-coated glasses a colored negative-decoration is produced. Filigree jewelry decoration on glass or ceramic articles are advantageously manufactured by engraving by means of laser beams (for example DD-PS 118251). For the manufacture of colored filigree positive decorations this laser-technology is not applicable.

In the Japanese patent disclosure JA49-4352 is proposed a laser-decoration process for the manufacture of colored pictures on glass or ceramic articles where the intended colored picture is applied to the article to be decorated and is afterwards fixed by means of a laser beam that directly illuminates the entire picture surface. The disadvantage of this process is that it has been found that the desired painting can only be applied to an even surface as by means of screen printing;

requiring on one hand that it must be hand painted on and on the other the subsequent Pixierung [*pixelation, spot irradiation?*] must be by an energy intensive laser of extremely high performance with the corresponding radiation diameters of the picture-surface. This necessitates a high financial expenditure in the present day state of laser technology, so that an economical process operation is not possible by this means.

Goal of this invention

The goal this invention is an enhancement of glass and ceramic articles through the application of a more abrasion-resistant filigree colored decoration in as economical way as possible.

Explanation of the nature of this invention.

The goal of this invention is a process for the manufacture of filigree gravure-like colored decoration by the use of the laser technology.

In accordance with this invention, the glass or ceramic article is coated with coloring, as well as colored materials, such as metal oxides, metal nitrides, color frits, and metal salts, and by the processing on the to be formed decoration, are fixed by the effect of a fine-focused laser beam with an output performance of 20-200 watts, without which a damage of the material occurs on the object to be decorated. Beside using the colorant pigment in the form of a suspension, it can also be applied by dusting on the glass or ceramic article coated with a binder layer or through the electrostatic treatment of the article provided with a conductive coating.

Implementation examples

The invention is explained in more detail by the following implementation examples, with which this invention is not restricted to these examples.

Example 1

A colorless glass stemware was turned slowly on a turntable about its longitudinal axis. By means of a suitable nozzle, it is coated with a 20mm wide strip of a cup with a CoO-containing suspension. After the coating, it was gewobbelt [*wobbled?*] on a Brennfleck [*fire tip, focal point?*] of a 0.25mm^2 beam of a 200 watt fine-focused CO₂-laser, with the help of a saw-tooth impulse generator, over the 20mm wide area so that the meandering dark-blue decoration formed a filigree on the glass. The remaining suspension was washed off and was returned for reprocessing.

Example 2

A glass strand was coated 20mm below the lip-edge with about a 40mm wide binder layer. Afterwards, a dark-green colored glass frit was dusted on. A metal mask with a grape foliage pattern was pushed over the glass. Subsequently, the metal mask was irradiated on a turntable

with a slow elevation by means of the laser described under example 1. After removal of the mask and removing of the surplus color frit including the binder, the glass displayed a sharply defined dark-green grape foliage decoration that was produced through the metal pattern.

Example 3

A flat ceramic bowl was coated with a brown colored melt-suspension and was afterwards turned slowly on a turntable. The laser beam as described under example 1 was mechanically *gewobbelt* [wobbled?] and generated a sinusoidal dark brown filigree pattern on the wall surface of the ceramic bowl. The unused color melt was again removed

The decoration manufactured according to this invention, as opposed to screen printing, showed a significantly higher abrasion resistance so that even after multiple mechanical cleaning the glass, as well as ceramic, articles showed no faulty sites existing in the decoration.

Invention claims

1. Processes for the application of colored decorations to glass or ceramic articles thereby characterized in that colored pigments are deposited on the article to be decorated and afterwards, under the application a fine-focused laser beam with an output-power of 20-200 watts, which is directed in such a manner so as to fix it onto the glass or ceramic articles, without which a material loss takes place on the object to be decorated.
2. Processes according to point 1 thereby characterized in that the direction of the laser beam takes place through a pattern or directed by a lens between the laser source and the article to be decorated.
3. Processes according to point 1 thereby characterized in that metal salts, oxides, nitrides or color frits are used as coloring pigments.
4. Processes according to point 1 thereby characterized in that the application of the coloring pigments occurs by coating with a suspension, by spraying out of corresponding solutions, by dusting of powders having suitable grain size onto articles previously coated with binders or through electrostatic deposition onto the article provided with a conductive coating.

Translated from the German
by Dr. Max Roha
October 1, 1998

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